

## VII. SUMMARY

The following is a summary of the state of knowledge with respect to the different elements of the natural barrier for radionuclide transport at Yucca Mountain: groundwater chemistry, radionuclide solubility, sorption, and diffusion. We also include summaries of material from the related Yucca Mountain Site Characterization Project milestones of “Summary and Synthesis of Biological Sorption and Transport” (#3663) and “Specific Interaction Theory Studies” (#3792M).

### A. BIOLOGICAL SORPTION AND TRANSPORT (MILESTONE #3363)

The results of research performed as part of the Biological Sorption and Transport Task of the Yucca Mountain Site Characterization Project have been presented in a report on milestone #3663 (Hersman 1996). These studies reveal that microorganisms can affect transport in several ways.

- Based only on the relative concentration of microorganisms in the two studies (laboratory and field), it is tempting to predict that the effect of the indigenous population on the sorption of  $^{239}\text{Pu}(\text{IV})$  would be negligible, and for one to conclude that the indigenous population will do little to retard the transport of plutonium by biosorption. However, the design of the laboratory experiment represents only a static, small location within the mountain. As the waste plume moves from one sorption location to the next, a continuum of sorption is occurring, with each site sorbing 0.075 times as much as it would if it were sterile, or by a factor of 1.075. Therefore, the affects of microbial sorption would enhance the sorption characteristics of the mountain by 7.5 per cent.
- Estimates suggest that the indigenous population of microorganisms is capable of producing enough chelating agents (for example, siderophores) to chelate 0.2 g/l of  $^{239}\text{Pu}$  in the subsurface pore water. Because this amount exceeds the solubility of plutonium, there is a significant potential for siderophores to increase the transport of actinide elements.
- Based on the results of laboratory studies, microorganisms increased significantly the rate of colloidal agglomeration. The field studies suggest that there are enough microorganisms present to affect similarly the agglomeration of individual colloids, indicating that the indigenous population should reduce the colloidal transport of radioactive wastes.
- Field and isotopic analysis indicate that the elevated subsurface carbon-dioxide concentrations are the result of biogenic activity. Elevated carbon-dioxide levels will affect transport by lowering the pH of the pore water, thereby increasing the solubility of most actinide elements. Also, lowering the pH will promote the dissolution of minerals, such as calcite, that are important in the retardation of actinides.
- Samples collected along the Exploratory Study Facility (ESF) contain a small population of microorganisms that is metabolically active and responsible for the production of the elevated levels of subsurface carbon dioxide. Analysis also revealed that this population was significantly affected by anthropogenic disturbances, increasing nearly four fold from the time of initial sampling. It is important, therefore, that the population within the ESF be monitored routinely to assess the effects of construction activities on their numbers and types.
- It is not possible to quantify the overall potential for the indigenous population to affect transport. However, a cautious and qualitative interpretation of this work indicates that there

is a strong potential for the subsurface population to promote the transport of radionuclide wastes, based on the dominant potential for chelation and carbon-dioxide production to accelerate transport. However, more work is needed before these results can be quantified.

## B. GROUNDWATER CHEMISTRY (CHAPTER II)

The chemical compositions of pore waters, perched waters, and saturated-zone groundwaters suggest there are basically two types of waters in Yucca Mountain.

- Type-1 water occurs as pore waters in hydrologic units mainly above, but also below, Tuff of Calico Hills. This water type generally has higher ionic strength than type-2 waters and is strongly influenced by soil-zone processes such as the precipitation of calcite, gypsum, and silica.
- Type-2 water occurs as perched waters and saturated-zone groundwaters. This water type is more dilute and is strongly influenced by hydrolysis reactions involving carbonic acid.
- Pore waters in Tuff of Calico Hills appear to be mixtures of the two basic water types, that is, pore waters from the overlying Topopah Spring Tuff and perched waters.
- The chemical data indicate that the equilibration of pore waters and perched or groundwaters is a very slow process.
- Future compositional variations in water chemistry under ambient conditions are likely to be of minor magnitude.
- The compositions of the J-13 and UE-25 p#1 waters appear to bound most of the compositional variations to be expected in the ambient flow system at Yucca Mountain in the future.

The main parameters not entirely bounded by these compositions are pH, Eh, and chloride concentrations.

- The uncertainty in the identity of alteration phases that control the type-2 water compositions and the lack of experimental data on the kinetics of formation of possible alteration phases preclude the development of realistic quantitative models of water chemistry in Yucca Mountain.

## C. SOLUBILITY AND SPECIATION (CHAPTER III AND MILESTONE #3792M)

- The carbonate anion is an exceptionally strong complexing agent for actinide ions and is present in significant concentrations in waters characteristic of the Yucca Mountain region.
- The ability of some actinide cations to hydrolyze water requires that any aqueous model of actinides in Yucca Mountain groundwaters include thermodynamic descriptions of hydroxo, carbonato, and mixed hydroxo-carbonato complexes. The details of this work are given in a report on milestone #3792M (Tait 1996).
- The solubility of neptunium, plutonium, and americium will depend on solution speciation (especially with  $\text{OH}^-$  and  $\text{CO}_3^{2-}$ ) and the solubility-limiting solid.
- Bulk solubility experiments can provide empirical data directly, but because they are long-term experiments, only a limited number of data points can be collected over a limited range of conditions. To determine solubility for general conditions, the system must be modeled thermodynamically.
- Bulk solubility of neptunium in J-13 water ranges from  $6 \times 10^{-6} \text{ M}$  to  $10^{-3} \text{ M}$ ; the solubility-limiting solid was predominately (but

not exclusively)  $\text{Np}_2\text{O}_5$ .

- For water conditions expected at Yucca Mountain, the data for Np(V) solutions is consistent, and modeling with the EQ3/6 code suggests a combination of  $\text{NpO}_2^+$  and  $\text{NpO}_2\text{CO}_3^-$  as the dominate species.
- Recent modeling work at Los Alamos indicates Np(IV) solids may form in Yucca Mountain waters depending on which solid-state numbers are used. The importance of this observation is that Np(IV) solids may be much less soluble than the Np(V) currently considered in performance assessment calculations.
- Bulk solubility of plutonium in J-13 water extends over a relatively narrow range from  $4 \times 10^{-9}$  to  $5 \times 10^{-8}$  M; the predominate solubility-limiting solid is Pu(IV)-oxide polymer at 25°C, aging to more crystalline  $\text{PuO}_2(\text{s})$  at 90°C.
- In the model, plutonium speciation is calculated to be dominated by  $\text{Pu}(\text{OH})_5^-$  in J-13 water, and the solids  $\text{PuO}_2(\text{s})$  and  $\text{Pu}(\text{OH})_4(\text{s})$  are calculated to be supersaturated to saturated.
- The bulk solubility of americium ranges from  $3 \times 10^{-10}$  to  $4 \times 10^{-6}$  M; the solubility limiting solid was reported to be a mixture of hexagonal and orthorhombic forms of  $\text{AmOHCO}_3$ , but this assertion is controversial and more work would need to be done to confirm or reject the statement.
- Only preliminary modeling of americium has been done. The predominate solution species was calculated to be  $\text{AmCO}_3^+$  in J-13 water except at 90°C and pH-8, in which case the dominant species was calculated to be  $\text{Am}(\text{CO}_3)_2^-$ . Furthermore, the hydroxo solids  $\text{Am}(\text{OH})_3$  and  $\text{Am}(\text{OH})_3(\text{amorphous})$  were calculated to be significantly below saturation throughout the experimental conditions for the

bulk solubility study. The only solid to approach saturation in the calculations was  $\text{AmOHCO}_3$ .

## D. SORPTION (CHAPTER IV)

- The elements niobium, tin, thorium, and zirconium show strong sorption onto surfaces available in Yucca Mountain rock units. In addition, these elements form solid oxides and hydroxides that have very low solubilities in Yucca Mountain groundwaters. In near-neutral solutions, they are fully hydrolyzed. A minimum sorption-coefficient value of 100 ml/g is appropriate in performance-assessment calculations for all these elements under essentially all conditions expected within the Yucca Mountain flow system.
- The elements actinium, americium, and samarium also sorb strongly to surfaces in Yucca Mountain rock units. These elements tend to form carbonates, phosphates, and mixed hydroxycarbonate compounds that are very sparingly soluble. A minimum sorption-coefficient value of 100 ml/g is appropriate for each of these elements.
- Plutonium's solution and sorption behavior are the most complex of all the elements of interest. The groundwater compositional parameter most critical to this element in the Yucca Mountain flow system is the redox potential, Eh. The available sorption data suggest that this element should sorb strongly to Yucca Mountain tuffs under most of the expected conditions. However, because in the experiments to date, the redox potential was not controlled, additional controlled experiments should be carried out. The recommendation is to bias the redox potential to a high level in a series of sorption experiments using several rock types and a water composition representative of the unsaturated zone. If the sorption coefficients obtained in these experi-

ments are consistent with earlier results, plutonium can be classified with the strong sorbers and a minimum sorption-coefficient value of 100 ml/g could be used in performance-assessment calculations. On the other hand, if the sorption coefficients are decreased by the elevated redox potential imposed, then additional experiments will need to be carried out to better define the appropriate range of the sorption coefficient to be used in the calculations.

- Cesium and radium have high affinities for most Yucca Mountain rock samples, particularly zeolitic samples. A minimum sorption-coefficient value of 100 ml/g could be used for these elements assuming that cesium concentrations in solution stay below  $10^{-5}$  M. For strontium, the situation is more complex. Although this element has a high affinity for zeolitic samples, it is not strongly sorbed by devitrified and vitric tuffs. Because the zeolitic tuffs will be a strong barrier for this element, the small sorption-coefficient values obtained to date for this element could be used for devitrified and vitric units.
- The sorption coefficient data available for the elements nickel and lead are limited to a dozen or so experiments on nickel. In the surficial environment, lead appears to be less mobile than nickel. Therefore, the nickel sorption coefficients can be used as default values for lead. In devitrified and zeolitic zones, a minimum sorption-coefficient value of 100 ml/g is appropriate for nickel. In vitric zones, sorption coefficients will be in the range from 0 to 50 ml/g. For vitric zones, it is recommended that performance-assessment calculations use a random sampling technique to derive nickel and lead sorption coefficients from a normal distribution ranging from 0 to 50 ml/g.
- The group that includes the elements neptunium, protactinium, selenium, and uranium is the most difficult to deal with because the sorption affinities for this group are generally small. Neptunium appears to sorb primarily by surface-complexation and surface-precipitation mechanisms. The carbonate content of the rocks used in experiments with neptunium appear to have a large impact on sorption behavior. The presence of ferrous iron on surfaces in the tuffs may also be a factor. The recommendation is to oxidize the samples prior to use in sorption experiments to passify any ferrous iron that may be present on surfaces. If this does not affect the sorption coefficient for the rock, a very weak acid leach should be used to remove potential carbonate minerals. If this also has minimal effect, then the presently available sorption-coefficient data could be used for performance-assessment calculations. If either of these procedures results in the lowering of the sorption affinity, additional steps will have to be taken to derive appropriate sorption coefficients.
- Protactinium appears to be very insoluble in near-neutral solutions, but its sorption behavior is more complicated. At high pH, protactinium appears to sorb strongly, whereas just below neutral pH, it sorbs poorly. Because only lower-range pH experiments have been conducted with Yucca Mountain samples to date, the recommendation is to carry out several experiments in the higher pH range.
- Selenium will be present as an anion in Yucca Mountain flow systems and will have low sorption affinity. The main unresolved issue is the effect of elevated levels of calcium and magnesium on its sorption behavior. The recommendation is to carry out several additional sorption experiments with selenium using a water with relatively high amounts of calcium and magnesium.
- Uranium sorption appears to be controlled by pH, alkalinity, and alkaline-earth-ion concentrations. Its affinity for Yucca Mountain rock

samples is generally low with the highest sorption coefficients observed in zeolitic tuffs. The main gap in the available data is for sorption coefficients on zeolitic and devitrified samples in contact with water enriched in calcium and magnesium at pH values from 6.5 to 8.0. The recommendation is to carry out two sets of experiments: one with a water high in calcium and magnesium but low in alkalinity; the other with a water high in calcium, magnesium, and alkalinity (for example, UE-25 p#1 water). Both a zeolitic and a devitrified sample should be tested.

- The final group includes the elements carbon, chlorine, iodine, and technetium. These elements have little or no sorption affinity under the oxidizing conditions expected within the Yucca Mountain flow system. Any retardation of these will involve processes other than sorption.
- In a batch-sorption study of the effect of naturally occurring organic materials on the sorption of cadmium and neptunium on oxides and tuff surfaces, the model sorbents were synthetic goethite, boehmite, amorphous silicon oxides, and a crushed tuff material from Yucca Mountain, Nevada. An amino acid, 3-(3,4-dihydroxyphenyl)-DL-alanine (DOPA), and an aquatic-originated fulvic material, Nordic aquatic fulvic acid (NAFA), were used as model organic chemicals. DOPA and NAFA have little effect on neptunium sorption on all sorbents selected for study.

## E. TRANSPORT AND DIFFUSION (CHAPTERS V AND VI)

Batch-sorption techniques yield sorption coefficients that appear to predict radionuclide transport under saturated and unsaturated conditions (at the laboratory scale) conservatively. These techniques need to be supplemented with dynamic transport and diffusion experiments.

- The Unsaturated Flow Apparatus (UFA) is a useful technique to assess the validity of batch-sorption coefficients. However, it would be practically impossible to measure all the necessary  $K_d$  values using the UFA approach because of the amount of time required for such an effort (as a result of the extremely low conductivities of the Yucca Mountain tuffs).
- The exclusion of anions such as pertechnetate in the vitric, devitrified, and zeolitic crushed tuffs we studied is almost negligible except in the case of zeolitic tuffs in J-13 water. In this case, the anion exclusion of pertechnetate in zeolitic tuffs is small but measurable.

To assess colloid-facilitated radionuclide transport in groundwaters at the potential nuclear waste repository at Yucca Mountain, it is very important to understand the generation and stability of colloids, including naturally occurring colloids.

- The colloid concentration in waters from Well J-13 was measured to be on the order of  $10^6$  particles/ml (for particle sizes larger than 100 nm). At this low particle loading, the sorption of radionuclides to colloids would have to be extremely high before the colloids could carry a significant amount of radionuclides from the repository to the accessible environment.

Diffusion is one of the most important retardation mechanisms in fractured media.

- The diffusion of nonsorbing radionuclides into saturated devitrified tuff is slower than diffusion into saturated zeolitic tuffs. The diffusion of tritiated water through saturated devitrified tuffs is on the order of  $10^{-6}$  cm<sup>2</sup>/s.
- Large anions, such as the neptunyl-carbonato complex or pertechnetate, are excluded from the tuff pores because of their size and charge. The diffusion coefficients for pertechnetate in saturated tuffs are on the order of  $10^{-7}$  cm<sup>2</sup>/s.

- The use of the Unsaturated Flow Apparatus is the most efficient and cost effective way of studying diffusion as a function of saturation in Yucca Mountain tuffs.

Calculations of radionuclide transport often include assumptions about fast pathways, such as fractures, that are too simplistic. This approach leads to overconservative predictions of radionuclide releases to the environment.

- Our results indicate that diffusion from the fracture into the matrix can take place even at relatively fast flow rates.
- Neptunium can be significantly retarded, even during a fracture-flow scenario. Neptunium retardation in fractures could be due to both diffusion into the matrix and sorption onto the minerals lining the fracture walls